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Mathematical Modelling and Numerical Analysis Will be set by the publisher
Modélisation Mathématique et Analyse Numérique

RELAXATION MODELS OF PHASE TRANSITION FLOWS

Philippe HELLUY[1] and Nicolas SEGUIN[2]

Abstract. In this work, we propose a general framework for the construction of pressure law for phase transition. These equations of state are particularly suitable for a use in a relaxation finite volume scheme. The approach is based on a constrained convex optimization problem on the mixture entropy. It is valid for both miscible and immiscible mixtures. We also propose a rough pressure law for modelling a super-critical fluid.

Résumé. Dans ce travail, on propose un cadre général pour construire des lois de pression pour les fluides subissant des transitions de phase. Ces lois de pression sont particulièrement adaptées aux schémas numériques de relaxation. L'approche est basée sur la résolution d'un problème d'optimisation convexe avec contraintes sur l'entropie du mélange. Les mélanges miscibles ou immiscibles peuvent être traités par cette approche. Nous proposons enfin un modèle très simple de fluide super-critique.

1991 Mathematics Subject Classification. 76M12, 65M12.

december 2005.

Introduction

The Euler equations of compressible inviscid flows possess strong non-linearities that lead to the possibility of several discontinuous solutions. It is then necessary to take into account a dissipative mechanism to select a unique solution. The most classical selection criterion is the Lax entropy criterion [21] that expresses, in a weak sense, the growth of the physical entropy. In order to converge towards the entropy solution, numerical methods have also to take into account a discrete version of the entropy criterion. Among the huge quantities of methods that have been proposed to approximate the Euler system, the relaxation approach has proved to be very interesting both on the theoretical and the practical sides [6], [29], [11], [30], [23], [10], [1], [13], [5], [2], [9] *etc.* The principle is to consider an augmented system, with more unknowns, that is in some sense "more linear" than the original Euler system. Then, appropriate source terms depending on a relaxation parameter λ are added to the augmented system. These source terms have two main features:

- when the parameter $\lambda \to \infty$, the augmented system tends, at least formally, towards the Euler system;
- they are compatible with the growth of the entropy.

Practically, a relaxation model leads to a very natural splitting method to approximate the Euler system. Each time step of the method is made of two stages. In the first stage, the augmented system is numerically solved without the source term. This resolution is simpler than for the Euler system. In the second stage, the source terms are applied.

Keywords and phrases: finite volume, entropy optimization, relaxation, phase transition, reactive flows, critical point.

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In this paper, we concentrate on a compressible flow with phase transition. For simplicity, but without a loss of generality, we restrict to one-dimensional problems. The considered relaxation model is the following

$$\begin{aligned} &\rho_t + (\rho u)_x = 0, \\ &(\rho u)_t + (\rho u^2 + p)_x = 0, \\ &(\rho\varepsilon + \rho u^2/2)_t + ((\rho\varepsilon + \rho u^2/2 + p)u)_x = 0, \\ &Y_t + uY_x = -\lambda(Y - Y_{eq}). \end{aligned} \tag{1}$$

The unknowns are the density $\rho > 0$, the velocity u, the internal energy $\varepsilon > 0$ and the vector of fractions $Y \in [0,1]^3$, all depending on the space variable x and the time variable t. The vector of fractions is of the form $Y = (\varphi, \alpha, z)^T$, where φ is the vapor mass fraction, α is the vapor volume fraction and z is the vapor energy fraction. The pressure p is a function of the specific volume $\tau = 1/\rho$, the internal energy ε and the vector of fractions Y. It is defined *via* the specific entropy function $s : (\tau, \varepsilon, Y) \to s(\tau, \varepsilon, Y)$. The specific entropy satisfies:

$$\begin{aligned} &\text{For all } Y, \quad (\tau,\varepsilon) \to s(\tau,\varepsilon,Y) \text{ is strictly concave;} \\ &\text{For all } (\tau,\varepsilon), \quad Y \to s(\tau,\varepsilon,Y) \text{ is strictly concave;} \\ &\text{For all } (\tau,\varepsilon,Y), \quad s_\varepsilon(\tau,\varepsilon,Y) > 0. \end{aligned} \tag{2}$$

It also gives the form of the pressure law

$$p := \frac{\partial s/\partial\tau}{\partial s/\partial\varepsilon}. \tag{3}$$

The relaxation parameter λ is > 0. More generally, one can also consider that λ is a symmetric ≥ 0 matrix. The equilibrium vector of fractions Y_{eq} is defined by

$$s(\tau,\varepsilon,Y_{eq}(\tau,\varepsilon)) = \max_{0\leqslant Y\leqslant 1} s(\tau,\varepsilon,Y). \tag{4}$$

With the previous conditions and definitions, the relaxation model (1) appears to be hyperbolic. The quantity $U = -\rho s$ is a Lax entropy of (1) associated to the entropy flux $G = -\rho u s$. The positivity of λ and the concavity of s with respect to Y implies that regular solutions of the system satisfies the second principle of thermodynamics

$$s_t + us_x \geq 0. \tag{5}$$

In a previous paper [2], we have proposed possible forms for the entropy $s(\tau, \varepsilon, Y)$. We have presented some numerical experiments and physical applications of the model (1). In the present work we concentrate on a procedure, inspired from the thermodynamics of mixtures, in order to design physically and mathematically coherent specific entropies $s(\tau, \varepsilon, Y)$.

Remark 1. *For a general theory of relaxation models we refer to [5]. Our relaxation system is not an entropy extension of the relaxed system in the sense of [11] because the entropy s is generally not concave with respect to all the variables* (τ, ε, Y) *(see conditions (2)). But it seems to comply with the reduced stability condition of [5]. The subcharacteristic property and the dissipativity of the leading term in the Chapman-Enskog expansion with respect to* $1/\lambda$ *are thus assured.*

The plan of this work is the following.

In Section 1 we first recall the thermodynamics theory for a single fluid. In the classical presentations of thermodynamics (as in [20], [8], [14], [28], [12]) the starting point is the entropy function of the fluid. The pressure and temperature laws are computed from the entropy.

In Section 2 we start to state a mathematical framework for the thermodynamics of mixtures. When two different fluids are mixed and if the entropies are known, it is possible to find the mixture entropy after the resolution of a convex optimization problem. The pressure law resulting from this computation is the well-known

isobaric law: at equilibrium, the pressure law is the common pressure of the two phases. It also appears that the mixture entropy is the sup-convolution of the entropies of the two phases. This fact is not difficult to notice but we have not found it in the classical literature. We then give a simple illustration of the previous theory. We compute the equilibrium of two phases satisfying the perfect gas law.

In Section 3, thanks to several numerical experiments, we will see that it is possible, in some cases, to capture several solutions satisfying an increasing entropy principle. This phenomenon is studied by Stéphane Jaouen in his thesis [19].

In Section 4 we show that the previous theory can also be applied to miscible mixtures. It can be done by only changing the constraints in the optimization problem. The resulting pressure law is then the Dalton law: the pressure of the mixture is the sum of the partial pressures of the two phases. We give a simple example. We also propose a tentative modelling of the critical behavior. The idea is to modify the constraints in such a way that the mixture becomes more and more "miscible" when the energy increases. With this very rough approach, we are able to recover some features of a critical behavior: bounded saturation line, saturation region ending up at a critical temperature.

1. Thermodynamics of a single fluid

1.1. **Entropy**

Consider a single fluid of mass $M \geq 0$, internal energy $E \geq 0$, occupying a volume $V \geq 0$. If the fluid is homogeneous and at rest, its behavior is entirely defined by its entropy function

$$S : (M, V, E) \to S(M, V, E). \tag{6}$$

In the sequel, we note $W = (M, V, E)$. The vector W belongs to a closed convex cone of R^3, $C = \{(M, V, E),$ $M \geq 0, V \geq 0, E \geq 0\}$. According to thermodynamics the entropy function must satisfy

- The entropy S is positively homogeneous of degree 1 (in short: "S is PH1")

$$\forall \lambda > 0, \quad S(\lambda W) = \lambda S(W). \tag{7}$$

- The entropy $S(W)$ is concave with respect to W.

The chosen axiomatic is justified in [8], [14]. In the sequel, we will sometimes suppose more regularity of $W \to S(W)$ (as the existence and the continuity of the partial derivatives of S). The two above conditions are equivalent to

$-S$ is sub-linear (see [18]).

The inverse of the temperature is defined by

$$\theta = \frac{1}{T} = \frac{\partial S}{\partial E}, \tag{8}$$

the pressure is

$$p = T\frac{\partial S}{\partial V}, \tag{9}$$

and the chemical potential (or the Gibbs specific energy) is

$$\mu = -T\frac{\partial S}{\partial M}. \tag{10}$$

In this way, we recover the classical relation

$$TdS = dE + pdV - \mu dM. \tag{11}$$

The Euler relation for PH1 functions reads

$$S(W) = \nabla S(W) \cdot W, \tag{12}$$

and this is nothing else than the Gibbs relation

$$\mu M = E + pV - TS. \tag{13}$$

The quantity $G = \mu M$ is called the Gibbs free energy. Usually, the PH1 functions of W are said *extensive*. The PH0 functions are said *intensive*. The gradient of a PH1 function being PH0, the temperature, the pressure and the chemical potential are necessarily intensive. It is also usual to define the specific entropy s by

$$Ms = S(M, V, E). \tag{14}$$

Because S is PH1, we see that s is PH0 (intensive) and that

$$s = S(1, \frac{V}{M}, \frac{E}{M}). \tag{15}$$

Therefore it is natural to consider the specific entropy s as a function of the specific volume $\tau = V/M$ and of the specific energy $\varepsilon = E/M$. The density is the inverse of the specific volume, $\rho = 1/\tau$. According to the context, we shall consider the intensive variables as functions of W or of (τ, ε). Setting $M = 1$ in the previous formula, we see that we also have

$$Tds = d\varepsilon + pd\tau. \tag{16}$$

Gibbs relation (13) can also be written

$$\mu = \varepsilon + p\tau - Ts. \tag{17}$$

Remark 2. *According to the Euler relation (12), the extensive entropy function S cannot be strictly concave. Indeed, the vector W is always in the kernel of $S''(W)$, where S'' is the Hessian matrix of S. If S is the entropy function of a single phase (a pure gas or a pure liquid for example) it is realistic to suppose that*

$$W \neq 0 \Rightarrow \dim \ Ker\ S''(W) = 1.$$

In this way, it can be proved, as in [12], that the specific entropy $(\tau, \varepsilon) \to s(\tau, \varepsilon)$, defined in (15), of a single phase is strictly concave. On the other hand, the specific entropy of a mixture is no longer strictly concave everywhere, as it will be seen below.

1.2. **Hyperbolicity**

Euler equations for a single fluid have the eigenvalues $u - c$, u and $u + c$, where u is the velocity of the fluid and c the sound speed. The sound speed depends on the pressure $p = p(\tau, \varepsilon)$

$$c^2/\tau^2 = pp_\varepsilon - p_\tau. \tag{18}$$

The sound speed is also expressed with the specific entropy $s(\tau, \varepsilon)$ by

$$\rho^2 c^2 = -T(p^2 s_{\varepsilon\varepsilon} - 2ps_{\tau\varepsilon} + s_{\tau\tau}). \tag{19}$$

Because the Hessian of s defines a negative quadratic form, we deduce from (19) that the system is hyperbolic if the temperature $T > 0$.

Remark 3. *The concavity of s implies the hyperbolicity of the Euler system, if the temperature is positive, with the corresponding pressure law. The concavity of s and the positivity of T are important conditions for a proper modelling. But the positivity of the pressure is absolutely not necessary. An example of a computation with negative pressure is proposed in [3].*

2. Immiscible Mixtures

In this paragraph, we present a classical model to describe the thermodynamics behavior of mixtures. With this model, it is possible to predict some characteristics of immiscible mixtures as the isobaric pressure law, and the existence of a saturation line for phase transition.

We consider two phases of a same pure body. Each phase is characterized by its own concave entropy function S_i, $i = 1, 2$, depending on the mass, volume and energy $W_i = (M_i, V_i, E_i)$. The two temperatures T_i are supposed to be always > 0. For simplicity, we will assume that the two resulting pressures p_i are also always positive. However, it would be interesting to study in detail the case where one of the two phases can support negative pressure for some specific volumes and energies.

2.1. **Optimization problem**

According to thermodynamics, the mixture entropy Σ is the sum of the two entropies. Out of equilibrium, it depends on $W_1 = (M_1, V_1, E_1)$ and $W_2 = (M_2, V_2, E_2)$ in the cone $C \times C$

$$\Sigma(W_1, W_2) = S_1(W_1) + S_2(W_2). \tag{20}$$

Let us now fix the mass, the volume and the energy of the mixture $W = (M, V, E)$. The conservations of mass and energy imply $M = M_1 + M_2$ and $E = E_1 + E_2$. If the two phases are immiscible, we also have $V_1 + V_2 \leq V$ (but more generally, for a mixture of gases for example, we only have $V_1 \leq V$ and $V_2 \leq V$. We will study the miscible case in Section 4).

The second principle of thermodynamics states that the system will evolve until the entropy reaches a maximum. The equilibrium entropy is thus given by

$$S(W) = \max_{(W_1, W_2) \in \Omega} \Sigma(W_1, W_2). \tag{21}$$

In this formula, the set $\Omega \subset C \times C$ is the set of constraints. If the two fluids are perfectly immiscible

$$(M_1, V_1, E_1, M_2, V_2, E_2) \in \Omega \Leftrightarrow \begin{cases} (M_1, V_1, E_1) \in C, \\ (M_2, V_2, E_2) \in C, \\ M_1 + M_2 = M, \\ V_1 + V_2 \leqslant V, \\ E_1 + E_2 = E. \end{cases} \tag{22}$$

The constraint set is a closed bounded convex set, which proves that the optimization problem is generally well posed (for this, it is sufficient that the opposites of the entropies $-S_i$ are lower semi-continuous functions). If the pressures p_1 and p_2 are always > 0, the constraint $V_1 + V_2 \leq V$ is necessarily saturated and can be replaced by $V_1 + V_2 = V$. Therefore, for positive pressure laws, the optimization problem becomes

$$S(W) = \max_{W_1 \in Q} S_1(W_1) + S_2(W - W_1). \tag{23}$$

The set of constraint is now $Q \subset C$

$$(M_1, V_1, E_1) \in Q \Leftrightarrow \begin{cases} 0 \leqslant M_1 \leqslant M, \\ 0 \leqslant V_1 \leqslant V, \\ 0 \leqslant E_1 \leqslant E. \end{cases} \tag{24}$$

The maximum can be reached on the boundary of the constraint set ∂Q or in the interior $\overset{\circ}{Q}$. When the maximum is in the interior $\overset{\circ}{Q}$ of the constraints set, which means that the two phases are present and at equilibrium, it corresponds to the physical saturation.

Remark 4. *The (mathematical) saturation of constraints should not be confused with the (physical) saturation that corresponds to the equilibrium of the two phases. Unfortunately, the classical terminology does not help here: for example, the mass constraint is (mathematically) saturated ($M_1 = M$ or $M_1 = 0$) when only one phase is stable* i.e. *when the mixture is not at (physical) saturation !*

We first give some generic indications on the computations of the maximum. More rigorous computations will be proposed below for perfect gases laws. When the maximum is in the interior of the constraint set, it is generally possible to compute the equilibrium by successive optimizations with respect to energy, volume and finally mass. We start with the optimization with respect to E_1. Because

$$\frac{\partial}{\partial E_1}\left(S_1(M_1, V_1, E_1) + S_2(M - M_1, V - V_1, E - E_1)\right) = 1/T_1 - 1/T_2, \tag{25}$$

the maximum is reached for $T_1 = T_2$.

The maximization with respect to V_1 leads to

$$\frac{\partial \Sigma}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0. \tag{26}$$

At equilibrium, because $T_1 = T_2$, the pressure law is thus isobaric

$$p = p_1 = p_2. \tag{27}$$

At this point, we have not yet taken into account the mass transfer (phase transition). We now focus on the optimization with respect to the mass M_1.

Proposition 1. *If the mixture is perfectly immiscible and if the pressures are >0, then, at equilibrium, the temperature, pressures and chemical potentials of the two phases are equal.*

Proof. We have already shown that for the immiscible model, the pressures and temperatures are equal at equilibrium. The equality of the chemical potentials comes from the cancellation of the derivative of Σ with respect to M_1.

$$\frac{\partial \Sigma}{\partial M_1} = -\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) = 0. \tag{28}$$

□

In most cases, the maximum of Σ is attained at a point W_1 on the boundary of the constraint set (see below). When the maximum is on the boundary ∂Q of the constraint set, it generally means that only one phase is stable. The maximum is then $(M_1, V_1, E_1) = (0, 0, 0)$ or $(M_1, V_1, E_1) = (M, V, E)$

Remark 5. *It would be interesting to study in detail models where only one or two constraints are saturated. For example one could imagine that the maximum is reached at a point (M_1, V_1, E_1) where $M > M_1 > 0, V_1 = 0, E > E_1 > 0$ (the phase (1) is present but occupies no volume). The conditions of such an equilibrium are $T_1 = T_2$, $\mu_1 = \mu_2$ but only $p_1 < p_2$.*

2.2. **Remarks on sup-convolution and Legendre transform**

In this short paragraph, we relate the equilibrium entropy given in (23) to classical operations in convex analysis, namely the sup-convolution operation and the Legendre transform. Although these links are not exploited in the sequel of the paper they may have an interest in the practical computation of equilibrium state

laws. As for the Fourier transform and the classical convolution, the Legendre transform and the sup-convolution can be computed by fast algorithms [7], [25], [26]. These algorithms could help to approximate the equilibrium pressure law when the analytical computations are not possible.

As explained before, the optimization problem (21), (22) can be restated as (23), (24) when the pressures are >0.

The reformulated problem reads

$$\begin{aligned} &S(W) = \max_{W_1 \in Q} S_1(W_1) + S_2(W - W_1), \\ &Q = \{(M_1, V_1, E_1), 0 \leqslant M_1 \leqslant M, 0 \leqslant V_1 \leqslant V, 0 \leqslant E_1 \leqslant E\}. \end{aligned} \tag{29}$$

It is classical to extend the entropies S_i outside the constraint set by

$$S_i(W) = \begin{cases} S_i(\mathrm{W}) \text{ if } W \in Q, \\ -\infty \text{ elsewhere.} \end{cases} \tag{30}$$

The equilibrium entropy is now defined by

$$S(W) = S_1 \square S_2(W) := \max_{W_1 \in R^3} \left(S_1(W_1) + S_2(W - W_1)\right), \tag{31}$$

where the symbol $\square$ is a notation for the sup-convolution operation in convex analysis. The sup-convolution operation enjoys many interesting properties ([17], [18]). There is an important link between the Legendre transform and the sup-convolution. The Legendre transform of the entropy is a concave function $W^* \to S^*(W^*)$ ($W^* \in R^3$) defined by

$$S^*(W^*) = \sup_W \left(W^* \cdot W + S(W)\right). \tag{32}$$

The sup-convolution is transformed into an addition by Legendre transform.

$$(S_1 \square S_2)^* = S_1^* + S_2^*. \tag{33}$$

Moreover, because the Legendre transform is involutive (for concave upper semi-continuous functions), we have

$$S_1 \square S_2 = \left(S_1^* + S_2^*\right)^*. \tag{34}$$

2.3. **Intensive variables**

It is often more convenient to solve the optimization problem with intensive variables. For this, let us define the volume fraction α, the mass fraction φ and the energy fraction z, between 0 and 1:

$$\alpha = \frac{V_1}{V}, \quad \varphi = \frac{M_1}{M}, \quad z = \frac{E_1}{E}. \tag{35}$$

We set

$$\begin{aligned} &s(\tau, \varepsilon, \alpha, \varphi, z) = \frac{1}{M}(S_1(M_1, V_1, E_1) + S_2(M_2, V_2, E_2)) \\ &= \varphi s_1(\tau \frac{\alpha}{\varphi}, \varepsilon \frac{z}{\varphi}) + (1 - \varphi) s_2(\tau \frac{1 - \alpha}{1 - \varphi}, \varepsilon \frac{1 - z}{1 - \varphi}). \end{aligned} \tag{36}$$

The specific entropy coming from formula (36) is the specific entropy out of equilibrium.

The equilibrium specific entropy is obtained after a maximization with respect to the fractions $Y = (\alpha, \varphi, z)$. The gradient of s with respect to the fractions is

$$\begin{aligned} s_\alpha &= \tau \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right), \\ s_\varphi &= - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right), \\ s_z &= \varepsilon \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \end{aligned} \tag{37}$$

If the maximum is in the interior of the constraint set, *i.e.* all the fractions Y_i satisfy $0 < Y_i < 1$, the gradient must be zero. We recover that the equilibrium corresponds to the equality of the pressures, temperatures and chemical potentials of the two phases. The mixture is saturated. But generally, the maximum is attained on the boundary of the constraints set $\alpha = \varphi = z = 0$ or $\alpha = \varphi = z = 1$ and only one phase is stable.

The derivatives of the out-of-equilibrium-entropy (36) with respect to τ and ε permits to define, at least formally, a pressure and a temperature of the mixture out of equilibrium. They depend on the volume τ and the energy ε, but also on the fractions (α, φ, z). They are given by

$$\begin{aligned} \frac{p}{T} &= \alpha \frac{p_1}{T_1} + (1-\alpha) \frac{p_2}{T_2}, \\ \frac{1}{T} &= z \frac{1}{T_1} + (1-z) \frac{1}{T_2}. \end{aligned} \tag{38}$$

2.4. **Example**

We give now a simple example. We consider two immiscible phases, each satisfying the perfect gas pressure law. More precisely, we choose as entropies (with $\gamma_1 > \gamma_2 > 1$)

$$s_i(\tau, \varepsilon) = \ln \varepsilon + (\gamma_i - 1) \ln \tau. \tag{39}$$

Setting

$$\gamma = \gamma(\varphi) = \varphi \gamma_1 + (1-\varphi) \gamma_2, \tag{40}$$

the mixture entropy is given by (36) that reads

$$\begin{aligned} s &= \ln \varepsilon + (\gamma - 1) \ln \tau \\ &+ (\gamma_1 - 1) \varphi \ln \alpha + (\gamma_2 - 1)(1-\varphi) \ln(1-\alpha) \\ &- \gamma_1 \varphi \ln \varphi - \gamma_2 (1-\varphi) \ln(1-\varphi) \\ &+ \varphi \ln z + (1-\varphi) \ln(1-z). \end{aligned} \tag{41}$$

The entropy is first optimized with respect to the energy fraction z. The maximum is always attained for $s_z = 0$ that implies $z = \varphi$. In the same way, the maximization with respect to α gives $\alpha = (\gamma_1 - 1)\varphi / (\gamma - 1)$. Before the maximization with respect to the mass fraction φ, the entropy looks like

$$\begin{aligned} s(\tau, \varepsilon, \varphi) = \ln \varepsilon + (\gamma - 1) \ln \left(\frac{\tau}{\gamma - 1} \right) + \\ \varphi (\gamma_1 - 1) \ln(\gamma_1 - 1) + (1-\varphi)(\gamma_2 - 1) \ln(\gamma_2 - 1). \end{aligned} \tag{42}$$

The maximization with respect to the mass fraction necessitates accounting for the constraint $0 \leq \varphi \leq 1$. Indeed,

$$\begin{aligned} s_\varphi(\tau,\varepsilon,\varphi) = (\gamma_1-\gamma_2)\ln\left(\frac{\tau}{\gamma-1}\right) + \\ (\gamma_1-1)\ln(\gamma_1-1) - (\gamma_2-1)\ln(\gamma_2-1) - (\gamma_1-\gamma_2). \end{aligned} \tag{43}$$

If $s_\varphi(\tau,\varepsilon,0) \leq 0$ then the maximum is at the point $\varphi = 0$, if $s_\varphi(\tau,\varepsilon,1) \geq 0$ then the maximum is $\varphi = 1$. In all the other cases, the maximum is reached at the unique φ_0, $0 < \varphi_0 < 1$, such that $s_\varphi(\tau,\varepsilon,\varphi_0) = 0$. This latter situation corresponds to a saturated mixture. The corresponding saturation curve in the (T,p) plane is a line

$$\frac{p}{T} = \exp\left(\frac{(\gamma_1-1)\ln(\gamma_1-1) - (\gamma_2-1)\ln(\gamma_2-1)}{\gamma_1-\gamma_2} - 1\right) = 1/\kappa. \tag{44}$$

The optimal value of φ is then defined by

$$\begin{aligned} \tau_1 &= (\gamma_1-1)\kappa, \\ \tau_2 &= (\gamma_2-1)\kappa, \\ \varphi_0 &= \frac{\tau-\tau_2}{\tau_1-\tau_2}. \end{aligned}$$

Because we have supposed $\gamma_1 > \gamma_2 > 1$, the optimized entropy is then

$$s(\tau,\varepsilon) = \begin{cases} \ln\varepsilon + (\gamma_2-1)\ln\tau & \text{if} \quad \tau \leqslant \tau_2 \\ \ln\varepsilon + \dfrac{\tau-\tau_2}{\kappa} + (\gamma_2-1)\ln\tau_2 & \\ = \ln\varepsilon + \dfrac{\tau-\tau_1}{\kappa} + (\gamma_1-1)\ln\tau_1 & \text{if} \quad \tau_2 \leqslant \tau \leqslant \tau_1 \\ \ln\varepsilon + (\gamma_1-1)\ln\tau & \text{if} \quad \tau \geqslant \tau_1 \end{cases} \tag{45}$$

The equilibrium pressure law is then

$$p(\tau,\varepsilon) = \begin{cases} (\gamma_2-1)\varepsilon/\tau & \text{if} \quad \tau \leqslant \tau_2, \\ \varepsilon/\kappa & \text{if} \quad \tau_2 \leqslant \tau \leqslant \tau_1, \\ (\gamma_1-1)\varepsilon/\tau & \text{if} \quad \tau_1 \leqslant \tau. \end{cases} \tag{46}$$

Remark 6. *Jaouen has established in [19] the pressure law (46), but with a different approach. He has also studied the Riemann problem for the Euler equations with this pressure law. He has shown that it is possible to find several entropy solutions to the Riemann problem. It is also possible to find several solutions satisfying the Lax characteristic criterion. Another selection criterion must be chosen. It is natural here to keep the Liu criterion [24]. Roughly speaking, the Liu criterion expresses that the good entropy solution is the one for which the production of entropy is maximal and it is equivalent to selecting shock waves that admit a viscous profile. The maximal entropy production criterion is frequent in many works. We refer for example to Mazet [27] for a numerical application.*

3. Numerical application

In this section, we present some numerical experiments. We try to approximate the formal limit when $\lambda \to \infty$ of the system (1). The limit is made of the Euler system

$$\begin{aligned} &w_t + f(w)_x = 0, \\ &w = (\rho, \rho u, \rho(\varepsilon + u^2/2))^T, \\ &f(w) = (\rho u, \rho u^2 + p, (\rho(\varepsilon + u^2/2) + p)u)^T, \end{aligned} \tag{47}$$

and the pressure $p = p(1/\rho, \varepsilon)$ is given by the formula (46).

The finite volume scheme is the one of Harten-Lax-van Leer (HLL) [15], of order 1, particularly simple to implement.

Let τ be a time step and h a space step. Let $t_n = n\tau$ and $x_i = ih$. The cells (or finite volumes) centered on the points x_i are defined by

$$C_i =]x_{i-1/2}, x_{i+1/2}[. \tag{48}$$

We look for an approximation w_i^n of $w(x_i, t_n)$ in the cell C_i at the time t_n. The approximation is given by the formula.

$$\frac{w_i^{n+1} - w_i^n}{\tau} + \frac{f_{i+1/2}^n - f_{i-1/2}^n}{h} = 0. \tag{49}$$

The numerical flux $f_{i+1/2}^n$ at the interface $i + 1/2$ is obtained by the HLL procedure. It depends on the left state $w_L = w_i^n$ and the right state $w_R = w_{i+1}^{n+1}$

$$f_{i+1/2}^n = f(w_i^n, w_{i+1}^n). \tag{50}$$

First, we define a minimal wave speed a and a maximal wave speed b at the interface between (L) and (R)

$$\begin{array}{l} a = \min\left(u_L - c_L, u_R - c_R\right), \\ b = \max\left(u_L + c_L, u_R + c_L\right), \end{array} \tag{51}$$

where c denotes the sound speed associated to the pressure law (46)

$$c(\frac{1}{\rho}, \varepsilon) = \left\{ \begin{array}{lll} \sqrt{\frac{\gamma_2 p}{\rho}} & \text{if} & \rho > \frac{1}{\tau_2}, \\ \frac{1}{\rho}\sqrt{\frac{p}{\kappa}} & \text{if} & \frac{1}{\tau_1} \leq \rho \leq \frac{1}{\tau_2}, \\ \sqrt{\frac{\gamma_1 p}{\rho}} & \text{if} & \rho < \frac{1}{\tau_1}. \end{array} \right. \tag{52}$$

We observe that the sound speed presents discontinuities at $\rho = 1/\tau_1$ and $\rho = 1/\tau_2$ and that it is smaller in the saturation region than in the pure phases.

Once the interface wave velocities have been defined, the HLL numerical flux is

$$f(w_L, w_R) = \left\{ \begin{array}{ll} f(w_L) & \text{if} \quad a \geq 0, \\ f(w_R) & \text{if} \quad b \leq 0, \\ \frac{bf(w_L) - af(w_R) + ab(f(w_R) - f(w_L)}{b-a} & \text{else.} \end{array} \right. \tag{53}$$

Let us now consider the maximal wave speed at time t_n

$$v_{\max}^n = \max_i \left(\left| a_{i+1/2}^n \right|, \left| b_{i+1/2}^n \right| \right). \tag{54}$$

The time step τ_n is chosen by

$$\tau_n = \delta \frac{h}{v_{\max}^n}, \tag{55}$$

where δ is the so-called CFL number.

We consider an initial condition corresponding to a Riemann problem found in [19], also used in [2]. The initial data are summed up in Table 1.

The considered Riemann problem has several entropy solutions (see [19], [28], [2]). The Liu solution, which corresponds to the maximal entropy dissipation, can be computed exactly. We compare the solution given by the HLL scheme with this exact solution.

A first computation whose data are given in Table 2 leads to the results of Figure 1. We observe that the Liu solution is well captured. The numerical production of entropy is ≥ 0.

Variable	left state	right state
density	$\tau_L = 0.92$	$\tau_R = 1.3$
velocity	$u_L = 0.4300665497$	$u_R = 0.3$
pressure	$p_L = 0.1445192299$	$p_R = 0.1$

TABLE 1. *Initial data, phase transition pressure law.*

Increasing slightly the CFL number δ leads to the results of Figure 2. This time, the scheme captures another solution. It is possible to affirm that this solution is also an entropy solution by examining the numerical production of entropy in the right shock, where the phase transition holds. This shock is solved on two cells. The entropy production in the right cell is positive. In the left cell, the production is negative. But globally, on the two cells, the production is positive. Thus, at convergence, the solution will be an entropy solution.

CFL δ	0.9418 or 0.9419
number of cells	1000
interval	$[-1/2, 1/2]$
final time	$t = 0.5$
pressure laws	$(\gamma_1 - 1) = 0.6, \quad (\gamma_2 - 1) = 0.5$

TABLE 2. *computation parameters.*

The programs that compute the HLL solution and the exact Liu solution can be downloaded at

`http://helluy.univ-tln.fr/phasetrans/index.html`

To our opinion, it is interesting to note that the construction procedure of the pressure law (46) has an incidence on the exact and numerical solutions of (47). It is also interesting that this behavior is observed with the HLL scheme, known to be highly entropy dissipative.

Intuitively, we explain the existence of several entropy solutions as follows. There are mainly two mechanisms that produce entropy: the admissible shock waves and the phase transition itself. We can imagine that an admissible shock wave, with positive entropy production, is balanced by a non-physical mass transfer between the two phases, with negative entropy production. In this way, we guess that it is possible to construct many entropy solutions to (47), (46).

Of course, it is possible to study directly the Riemann problem for (47), (46), as it is done for example in [19] and [28]. We think however that the underlying entropy optimization that leads to the pressure law (46) helps to understand the behavior of the solutions.

In [2] we have designed a relaxation scheme (different from the HLL scheme) for the approximation of this kind of problems. The main idea is to use a splitting method. Each time step is split into two sub-steps. In the first sub-step, a classical Godunov scheme is employed for a diphasic mixture without phase transition. The mixture variables (the fractions) are convected with the flow. The associated Riemann problem is much easier to solve, as proved in [3], [4]. In a second sub-step, the mixture variables are updated by optimizing the entropy with respect to the mixture variables. The convergence of the solution towards the Liu solution is numerically verified.

We must observe here that other selection criteria have been proposed. For example, with vanishing visco-capillary terms, it can be proved that the relevant solution is made of non-classical shock waves [22], [16]. There is still a debate to know which criterion (Liu's or visco-capillary) is physically the most relevant.

4. Miscible mixtures

As it can be checked in (44), the simple model does not present a critical behavior: the saturation curve is infinite in the (T, p) plane. We can wonder if it is possible to obtain a critical behavior (bounded saturation line) by considering more complex entropies s_1 and s_2.

We have made such an attempt in [2] to simulate water flows with cavitation. We chose stiffened gas entropies of the form

$$s_i = C_i \ln((\varepsilon_i - Q_i - \pi_i \tau_i)\tau_i^{\gamma_i - 1}) + s_i^0. \tag{56}$$

The law is characterized by several physical constants. The parameter C_i is the specific heat of fluid i. The parameter Q_i can be interpreted as a heat of formation. The parameter π_i has the dimension of a pressure and $-\pi_i$ is the minimal pressure for which the sound speed of fluid i vanishes. Although the resulting model can be made realistic for some ranges of pressures, it appears that it is not possible to get a critical behavior with the stiffened gas entropies. After several attempts with other laws, we now conjecture that our approach has to be slightly modified to model super-critical fluids.

One simple possibility that we will present in Section 4.3 is simply to modify the set of constraints in the optimization problem (22). But before presenting the method, we study the mixture of two miscible fluids.

4.1. **Optimization problem**

If the two fluids are perfectly miscible, they can both occupy the whole volume. The set of constraints is thus given by

$$(M_1, V_1, E_1, M_2, V_2, E_2) \in Q \Leftrightarrow \begin{cases} (M_1, V_1, E_1) \in C, \\ (M_2, V_2, E_2) \in C, \\ M_1 + M_2 = M, \\ V_1 \leqslant V, \\ V_2 \leqslant V, \\ E_1 + E_2 = E. \end{cases} \tag{57}$$

Consider now the optimization with respect to the volume variables V_1 and V_2 in this perfectly miscible case. The derivatives of Σ with respect to V_1 and V_2 are respectively p_1/T_1 and p_2/T_2. In a model where the pressures and temperature are >0, the maximum will be reached for a saturated constraint, i.e. for $V_1 = V_2 = V$. As in the immiscible case, the optimization with respect to the energy E_1 implies the temperature equilibrium. After the optimization with respect to V_1, V_2, E_1, E_2, the entropy has thus the form

$$\Sigma = S_1(M_1, V, E_1) + S_2(M - M_1, V, E - E_1), \tag{58}$$

the energy E_1 depending on the other variables

$$E_1 = E_1(M, V, E, M_1). \tag{59}$$

The equilibrium pressure is then given by the derivative of the equilibrium entropy

$$\frac{p}{T} = \frac{\partial \Sigma}{\partial V} = \frac{p_1}{T_1} + \frac{1}{T_1}\frac{\partial E_1}{\partial V} + \frac{p_2}{T_2} - \frac{1}{T_2}\frac{\partial E_1}{\partial V} \tag{60}$$

But at equilibrium, $T = T_1 = T_2$, and then we recover the Dalton law, which states that the mixture pressure is the sum of the partial pressures of the two fluids

$$p = p_1 + p_2. \tag{61}$$

Proposition 2. *If the mixture is perfectly miscible and if the pressures of the two phases are > 0, then, at equilibrium, $V_1 = V_2 = V$, $T_1 = T_2 = T$ and the pressure is $p = p_1 + p_2$ (Dalton law).*

4.2. **Example**

In this section we study the mixture of two miscible perfect gases. The entropies are

$$s_i = \ln(\varepsilon \tau^{\gamma_i - 1}). \tag{62}$$

In the miscible case, the two volume fractions are $\alpha_1 = \alpha_2 = 1$. According to (20) and (15) the mixture entropy is of the form

$$s(\tau, \varepsilon, \varphi, z) = \varphi s_1(\frac{\tau}{\varphi}, \frac{z\varepsilon}{\varphi}) + (1-\varphi) s_2(\frac{\tau}{1-\varphi}, \frac{(1-z)\varepsilon}{1-\varphi}). \tag{63}$$

A simple computation leads to

$$\begin{array}{l} s(\tau, \varepsilon, \varphi, z) = \ln \varepsilon + (\gamma - 1)\ln \tau + \varphi \ln z + (1-\varphi)\ln(1-z) \\ -\gamma_1 \varphi \ln \varphi - \gamma_2 (1-\varphi)\ln(1-\varphi), \\ \gamma = \varphi \gamma_1 + (1-\varphi)\gamma_2. \end{array} \tag{64}$$

And the optimization with respect to z leads to $z = \varphi$. Thus

$$\begin{array}{l} s(\tau, \varepsilon, \varphi) = \ln \varepsilon + (\gamma - 1)\ln \tau \\ -(\gamma_1 - 1)\varphi \ln \varphi - (\gamma_2 - 1)(1-\varphi)\ln(1-\varphi), \\ \gamma = \varphi \gamma_1 + (1-\varphi)\gamma_2. \end{array} \tag{65}$$

The maximum in φ is always reached for the unique solution $\varphi_0(\tau)$ of

$$\frac{\varphi^{\gamma_1 - 1}}{(1-\varphi)^{\gamma_2 - 1}} = \left(\frac{\tau}{\exp(1)}\right)^{\gamma_1 - \gamma_2}. \tag{66}$$

The optimal entropy is $s((\tau, \varepsilon, \varphi_0(\tau))$ and it has no simple expression.

Remark 7. *We observe that in this model, there is no saturation curve. Indeed, in contrast with the immiscible case, it is not possible to define a common pressure to the two components at equilibrium. The transition region from the fluid (1) to the fluid (2) is thus "diffused" in all the (T, p) plane.*

4.3. **Critical point**

In this section, we propose a simple approach in order to qualitatively model a critical behavior. The idea is to admit progressively a mixture covering of the two components when the energy of the mixture increases. In this way, we will pass from an immiscible model to a miscible one, and we have just seen that in the miscible model, the saturation zone is "diffused". The covering is obtained by altering the volume constraint $V_1 + V_2 \leqslant V$.

We consider two fluids characterized by their entropy functions, $S_i(W_i)$, $i = 1, 2$. Out of equilibrium, the mixture entropy is given by (20). However, the volume constraint is intermediate between (22) and (57).

$$(M_1, V_1, E_1, M_2, V_2, E_2) \in Q \Leftrightarrow \begin{cases} (M_1, V_1, E_1) \in C, \\ (M_2, V_2, E_2) \in C, \\ M_1 + M_2 = M, \\ E_1 + E_2 = E. \\ V_1 \leqslant V, \quad V_2 \leqslant V, \\ V_1 + V_2 \leqslant V + \eta E, \end{cases} \tag{67}$$

The parameter η is small, in such a way that for a small mixture energy E, the mixture behaves like an immiscible one. When the energy increases, the mixture becomes a miscible mixture. More precisely, when

$\eta E > V$, then the constraints $V_i \leq V$ are saturated, and we are exactly in the case of the miscible mixture. We have pointed out that for a perfectly miscible mixture, there is no more saturation line. We will see that with this model the saturation line is indeed bounded.

Remark 8. *It would be interesting to study other volume constraints in (67). For example, we could have replaced $V_1 + V_2 \leqslant V + \eta E$ by a more general inequality $V_1 + V_2 \leqslant V_0(M, V, E)$ where V_0 is a concave and PH1 function. Our choice is based on physical and complexity reasons.*

We have to study different cases for the optimization problem

$$S(W) = \max_{(W_1,W_2)\in Q} \Sigma(W_1, W_2). \tag{68}$$

First, the problem can be restated under the form: maximize

$$\Sigma = S_1(M_1, V_1, E_1) + S_2(M - M_1, V_2, E - E_1), \tag{69}$$

with respect to (M_1, V_1, V_2, E_1) under the constraints

$$\begin{aligned} &V_1 \leqslant V, \quad V_2 \leqslant V, \\ &V_1 + V_2 \leqslant V + \eta E. \end{aligned} \tag{70}$$

We first study the conditions for equilibrium of the phases. We will consider the case when the two phases exist and are at equilibrium. This means that the maximum of the mixture entropy is reached in the interior of the domain of constraints (at least for the mass and energy: the volume constraint can be saturated, as in the Dalton law).

Proposition 3. *If the two phases are present and at equilibrium then*

$$\begin{aligned} &T_1 = T_2 = \overline{T}, \\ &\mu_1 = \mu_2 = \overline{\mu}. \end{aligned} \tag{71}$$

Proof. The two phases are present when $0 < M_1 < M$ and $0 < E_1 < E$. The result is proved because

$$\begin{aligned} &\frac{\partial \Sigma}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2}, \\ &-\frac{\partial \Sigma}{\partial M_1} = \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}. \end{aligned} \tag{72}$$

□

We have now to maximize with respect to the volume. Different cases have to be considered. The first corresponds to $\eta E \leq V$ and the constraint $V_1 + V_2 \leqslant V + \eta E$ alone is saturated. Then, $V_2 = V + \eta E - V_1$.

Proposition 4. *If $\eta E \leq V$ and if $V_2 = V + \eta E - V_1$, then at equilibrium, we have also*

$$p_1 = p_2 = \overline{p}.$$

Proof. Now Σ reads

$$\Sigma = S_1(M_1, V_1, E_1) + S_2(M - M_1, V + \eta E - V_1, E - E_1) \tag{73}$$

The optimality condition reads

$$\frac{\partial \Sigma}{\partial V_1} = \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0, \tag{74}$$

and thanks to the previous proposition, we deduce $p_1 = p_2 = \overline{p}$. □

A very interesting feature of the proposed simple model is that the temperature, pressure and chemical potential of the equilibrium mixture *do not* correspond to the common temperatures, pressures and chemical potentials of the two phases. This fact can be stated more precisely thanks to the following proposition.

Proposition 5. *If $\eta E \leq V$ and if $V_2 = V + \eta E - V_1$, then at equilibrium, the temperature, pressure and chemical potential of the mixture are given by*

$$\begin{aligned} T &= \frac{\overline{T}}{1+\eta\overline{p}}, \\ p &= \frac{\overline{p}}{1+\eta\overline{p}}, \\ \mu &= \frac{\overline{\mu}}{1+\eta\overline{p}}, \end{aligned} \tag{75}$$

where $\overline{T}$, $\overline{p}$ and $\overline{\mu}$ correspond respectively to the common temperature, pressure and chemical potential of the two components at equilibrium.

Proof. At equilibrium, M_1, V_1 and E_1 depends on M, V, E in such a way that $T_1 = T_2 = \overline{T}$, $p_1 = p_2 = \overline{p}$ and $\mu_1 = \mu_2 = \overline{\mu}$. The mixture equilibrium temperature is then obtained from

$$\begin{aligned} &\frac{1}{T} = \frac{\partial \Sigma}{\partial E} = \frac{\partial}{\partial E}\left(S_1(M_1, V_1, E_1) + S_2(M - M_1, V + \eta E - V_1, E - E_1)\right) \\ &M_1 = M_1(M, V, E), \\ &V_1 = V_1(M, V, E), \\ &E_1 = E_1(M, V, E). \end{aligned} \tag{76}$$

It gives

$$\begin{aligned} &\frac{1}{T} = \frac{\partial M_1}{\partial E}\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) + \frac{\partial V_1}{\partial E}\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) + \\ &\frac{\partial E_1}{\partial E}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \eta\frac{p_2}{T_2} + \frac{1}{T_2} \end{aligned} \tag{77}$$

The conditions of equilibrium then give

$$T = \frac{\overline{T}}{1+\eta\overline{p}}.$$

The other expressions for the pressure and the chemical potential are obtained by similar calculations. □

Remark 9. *We observe that for the first case, in the "barred" variables, the saturation line is not different from the saturation line of the immiscible mixture. But the saturation line in the true pressure and temperature is obtained by a transformation $(\overline{T}, \overline{p}) \to (T, p)$ that maps an unbounded line to a bounded one. For example, the pressure is bounded by $p_c = 1/\eta$. This is nothing else than the desired qualitative critical behavior.*

We have now to study the transition from an immiscible to a miscible mixture. The next case corresponds to $\eta E \leq V$ and a maximum reached at a point where $V_1 = V$ and $V_2 = \eta E$ (and a symmetric case $V_2 = V$ and $V_1 = \eta E$).

Proposition 6. *In the case $\eta E \leq V$, if the maximum is reached for $V_1 = V$ and $V_2 = \eta E$ then the temperatures and chemical potentials of the two phases are equal (and noted as before $\overline{T}$ and $\overline{\mu}$). The mixture variables at equilibrium are*

$$\begin{aligned} T &= \frac{\overline{T}}{1+\eta p_2}, \\ p &= \frac{p_1}{1+\eta p_2}, \\ \mu &= \frac{\overline{\mu}}{1+\eta p_2}. \end{aligned} \tag{78}$$

A symmetric formula holds for the case $V_2 = V$, $V_1 = \eta E$.

Proof. Now Σ reads

$$\Sigma = S_1(M_1, V, E_1) + S_2(M - M_1, \eta E, E - E_1). \tag{79}$$

At equilibrium, the pressures are not necessarily the same, because the constraint on V_1 is saturated. The same kind of computations as in proposition 5 lead to the result. □

The last case corresponds to $\eta E > V$. Then necessarily $V_1 = V$ and $V_2 = V$. We are thus in the case of the perfectly miscible mixture and recover the Dalton law:

Proposition 7. *In the case $\eta E > V$, the maximum is reached for $V_1 = V_2 = V$. The temperatures and chemical potentials of the two phases are equal (and noted as before $\overline{T}$ and $\overline{\mu}$). The mixture variables at equilibrium are*

$$\begin{aligned} &T = \overline{T}, \\ &p = p_1 + p_2, \\ &\mu = \overline{\mu}. \end{aligned} \tag{80}$$

The computations can be made more precise with particular forms of the entropies and when the optimization problem is stated in intensive variables. The mixture specific entropy is given by

$$\sigma = \varphi s_1(\frac{\alpha_1}{\varphi}\tau, \frac{z}{\varphi}\varepsilon) + (1-\varphi)s_2(\frac{\alpha_2}{1-\varphi}\tau, \frac{1-z}{1-\varphi}\varepsilon). \tag{81}$$

The specific entropy has to be optimized with the constraints

$$\begin{aligned} &0 \leqslant z \leqslant 1, \quad 0 \leqslant \varphi \leqslant 1, \\ &0 \leqslant \alpha_1 \leqslant 1, \quad 0 \leqslant \alpha_2 \leqslant 1, \\ &\alpha_1 + \alpha_2 \leqslant 1 + \eta\rho\varepsilon. \end{aligned} \tag{82}$$

We consider the particular case of two perfect gas laws. The specific entropy is

$$\begin{aligned} &\sigma = \ln\varepsilon + (\gamma - 1)\ln\tau + \\ &\varphi \ln\frac{z}{\varphi} + \varphi(\gamma_1 - 1)\ln\frac{\alpha_1}{\varphi} + \\ &(1-\varphi)\ln\frac{1-z}{1-\varphi} + (1-\varphi)(\gamma_2 - 1)\ln\frac{\alpha_2}{1-\varphi}, \\ &\text{with } \gamma = \gamma(\varphi) = \varphi\gamma_1 + (1-\varphi)\gamma_2. \end{aligned} \tag{83}$$

We can simplify the expression of the entropy by expressing the temperature equilibrium

$$\frac{\partial\sigma}{\partial z} = 0 \Leftrightarrow z = \varphi,$$

and eliminating the energy fraction z. We find

$$\begin{aligned} &\sigma = \ln\varepsilon + (\gamma - 1)\ln\tau \\ &-\varphi(\gamma_1 - 1)\ln\varphi - (1-\varphi)(\gamma_2 - 1)\ln(1-\varphi) \\ &+\varphi(\gamma_1 - 1)\ln\alpha_1 + (1-\varphi)(\gamma_2 - 1)\ln\alpha_2, \\ &\gamma = \varphi\gamma_1 + (1-\varphi)\gamma_2. \end{aligned} \tag{84}$$

This expression has to be optimized for fixed ($\tau = 1/\rho, \varepsilon$) with respect to φ, α_1 and α_2. The constraints are

$$\begin{aligned} &0 \leqslant \varphi \leqslant 1, \\ &0 \leqslant \alpha_1 \leqslant 1, \quad 0 \leqslant \alpha_2 \leqslant 1, \\ &\alpha_1 + \alpha_2 \leqslant 1 + \eta\rho\varepsilon. \end{aligned} \tag{85}$$

As before, we start to optimize with respect to the volume fractions α_1 and α_2. For this purpose, when $\eta\rho\varepsilon \leq 1$, we introduce the two mass fractions that will correspond to the saturation of the constraints $\alpha_i = 0$ or $\alpha_i = 1$.

$$\begin{aligned} \varphi_{\min} &= \frac{\eta\rho\varepsilon(\gamma_2 - 1)}{\eta\rho\varepsilon(\gamma_2 - 1) + (\gamma_1 - 1)}, \\ \varphi_{\max} &= \frac{(\gamma_2 - 1)}{(\gamma_2 - 1) + \eta\rho\varepsilon(\gamma_1 - 1)}. \end{aligned} \tag{86}$$

If $\varphi_{\min} \leqslant \varphi \leqslant \varphi_{\max}$ then the maximum in α is

$$\begin{aligned} \alpha_1 &= \varphi \frac{\gamma_1 - 1}{\gamma - 1}(1 + \eta\rho\varepsilon), \\ \alpha_2 &= (1 - \varphi)\frac{\gamma_2 - 1}{\gamma - 1}(1 + \eta\rho\varepsilon). \end{aligned} \tag{87}$$

If $\varphi \leq \varphi_{\min}$ then the constraint $\alpha_2 \leq 1$ is saturated and we have

$$\begin{aligned} \alpha_1 &= \eta\rho\varepsilon, \\ \alpha_2 &= 1. \end{aligned} \tag{88}$$

If $\varphi \geq \varphi_{\max}$ then the constraint $\alpha_1 \leq 1$ is saturated and we have

$$\begin{aligned} \alpha_1 &= 1, \\ \alpha_2 &= \eta\rho\varepsilon. \end{aligned} \tag{89}$$

Finally, when $\eta\rho\varepsilon \geq 1$ the two constraints $\alpha_1 \leq 1$ and $\alpha_2 \leq 1$ are saturated and the maximum in α is simply $\alpha_1 = \alpha_2 = 1$.

The previous computations give the entropy before the optimization with respect to the mass fraction. If $\eta\rho\varepsilon \leq 1$ then:

- If $\varphi_{\min} \leqslant \varphi \leqslant \varphi_{\max}$ then

$$\begin{aligned} &\sigma = \ln\varepsilon + (\gamma - 1)\ln\frac{\tau + \eta\varepsilon}{\gamma - 1} + \\ &\varphi(\gamma_1 - 1)\ln(\gamma_1 - 1) + (1 - \varphi)(\gamma_2 - 1)\ln(\gamma_2 - 1). \end{aligned}$$

- If $\varphi \leq \varphi_{\min}$ then

$$\begin{aligned} &\sigma = \ln\varepsilon + (\gamma - 1)\ln\tau \\ &-\varphi(\gamma_1 - 1)\ln\varphi - (1 - \varphi)(\gamma_2 - 1)\ln(1 - \varphi) \\ &+\varphi(\gamma_1 - 1)\ln(\eta\rho\varepsilon). \end{aligned}$$

- If $\varphi \geq \varphi_{\max}$ then

$$\begin{aligned} &\sigma = \ln\varepsilon + (\gamma - 1)\ln\tau \\ &-\varphi(\gamma_1 - 1)\ln\varphi - (1 - \varphi)(\gamma_2 - 1)\ln(1 - \varphi) \\ &+(1 - \varphi)(\gamma_2 - 1)\ln(\eta\rho\varepsilon). \end{aligned}$$

If $\eta\rho\varepsilon \geq 1$ then

$$\sigma = \ln \varepsilon + (\gamma - 1)\ln \tau$$
$$-\varphi(\gamma_1 - 1)\ln\varphi - (1-\varphi)(\gamma_2 - 1)\ln(1-\varphi).$$

It can be checked that σ is of class C^1 with respect to φ.

The saturation region is the set of points where the temperature, pressure and chemical equilibriums hold. It implies that its boundary corresponds to the saturation of the volume constraints. It is thus defined by the two equalities

$$\begin{aligned} &\frac{\partial \sigma}{\partial \varphi}(\tau_2, \varepsilon, \varphi_{\min}) = 0, \\ &\frac{\partial \sigma}{\partial \varphi}(\tau_1, \varepsilon, \varphi_{\max}) = 0. \end{aligned} \tag{90}$$

These equalities define two functions $\tau_1(\varepsilon)$ and $\tau_2(\varepsilon)$ and the saturation region in the (τ, ε) plan is defined by

$$\tau_1(\varepsilon) \leq \tau \leq \tau_2(\varepsilon). \tag{91}$$

Defining the same constant κ as in (44)

$$\kappa = \exp\left(1 - \frac{(\gamma_1 - 1)\ln(\gamma_1 - 1) - (\gamma_2 - 1)\ln(\gamma_2 - 1)}{\gamma_1 - \gamma_2}\right),$$

we find

$$\begin{aligned} \tau_2 &= \kappa(\gamma_2 - 1) - \frac{\gamma_2 - 1}{\gamma_1 - 1}\eta\varepsilon, \\ \tau_1 &= \kappa(\gamma_1 - 1) - \frac{\gamma_1 - 1}{\gamma_2 - 1}\eta\varepsilon. \end{aligned} \tag{92}$$

The two curves τ_1 and τ_2 intersect at the critical point, for which $\eta\varepsilon/\tau = 1$. Then the critical specific volume τ_c satisfies $\kappa = \tau_c(\frac{1}{\gamma_1 - 1} + \frac{1}{\gamma_2 - 1})$.

It is more classical to express τ_1 and τ_2 with respect to the pressure. It is easily done using the equilibrium of temperatures and pressures in the saturation zone and on its boundary (see Proposition 5)

$$\begin{aligned} &T_1 = T_2 = \overline{T} = \varepsilon_1 = \varepsilon_2, \\ &\varepsilon = \varphi\varepsilon_1 + (1-\varphi)\varepsilon_2 = \overline{T}, \\ &p_1 = p_2 = \overline{p}, \quad T/p = \overline{T}/\overline{p} = \kappa, \\ &T = \frac{\overline{T}}{1 + \eta\overline{p}}, \quad p = \frac{\overline{p}}{1 + \eta\overline{p}}. \end{aligned}$$

In the saturation region, we thus have

$$\varepsilon = \kappa\frac{p}{1 - \eta p}. \tag{93}$$

In the (τ, p) plane, the left and right boundaries of the saturation region are

$$\begin{aligned} \tau_1 &= \kappa(\gamma_1 - 1) - \frac{\gamma_2 - 1}{\gamma_1 - 1}\eta\kappa\frac{p}{1 - \eta p}, \\ \tau_2 &= \kappa(\gamma_2 - 1) - \frac{\gamma_1 - 1}{\gamma_2 - 1}\eta\kappa\frac{p}{1 - \eta p}. \end{aligned} \tag{94}$$

It is not possible to give an explicit form of the pressure law. But by simple numerical computations, it is possible for example to draw the isothermal lines in the (τ, p) plane. They are represented on Figure 3

with $\gamma_1 = 1.4$ and $\gamma_2 = 1.1$. The Maple worksheet that permits to draw the Figure 3 is also provided on the above-mentioned web page.

The main qualitative behavior near the critical point is recovered:

- bounded saturation region in the (τ, p) plane;
- existence of a bounded saturation line in the (T, p) plane;
- the pressure is constant along the isothermal lines in the saturation region.

However some features, found in the van der Waals model for example [19], [9], are still missing:

- $\frac{\partial p}{\partial \tau} \neq 0$ at the intersection of the two curves τ_1 and τ_2;
- $p(\tau_2)$ is decreasing. For real material is should be increasing (but in practice, it is almost vertical);
- The pressure admits a jump on the line $\eta\varepsilon/\tau = 1$ instead of being continuous.

Let us repeat that our model is very simple. It is certainly possible to add more details to each single fluid entropy law as: heat capacities, heat of formation, reference entropies. Maybe it is then possible to recover the missing features.

Let us also mention that it's worth it because our model is also valid out of equilibrium unlike the van der Waals model that is a purely equilibrium model.

Conclusion

In this work, we have proposed a review of some results of the thermodynamics of mixtures. The computation of the equilibrium of two phases can be formulated as a constrained optimization problem on the mixture entropy. Many results are classical, but to our opinion, are not so clearly stated in the literature. Some remarks seem to be new:

- it appears that the equilibrium entropy is the sup-convolution of the entropies of the two phases. This can lead to many interesting applications related to fast Legendre transform algorithms;
- the isobaric law and the Dalton law can be rigorously proved by changing the constraints in the entropy optimization problem;
- one can define in a very natural way an entropy, and thus a pressure and a temperature, for a mixture out of equilibrium. We have thus to our disposal models for the dynamics of the phase transition. It would be interesting to compare the physical validity of such models with the classical model of metastability of van der Waals.

We have seen that the optimization problem is much easier to understand, on the theoretical side, when it is stated in extensive variables. However, for CFD applications and the coupling with Euler equations, it is necessary to state it in intensive variables.

Finally, we have given a tentative modelling of a super-critical fluid. We proposed a very simple modification of the constraints in the optimization of the entropy. With this modification, the mixture is more and more miscible when the energy increases. Some qualitative properties of super-critical fluids are recovered: bounded saturation line, horizontal isotherms in the saturation zone, *etc.* Investigations are still needed to obtain a more precise model for super-critical fluids.

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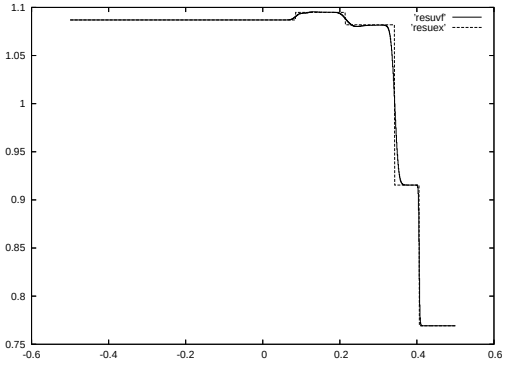
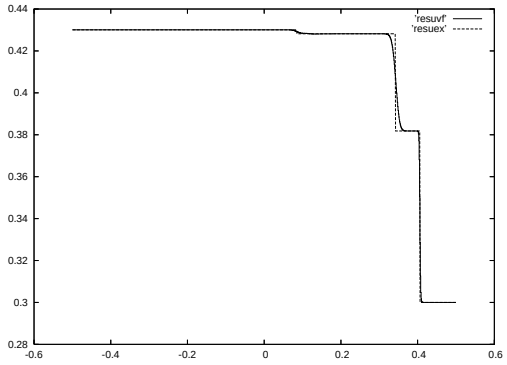
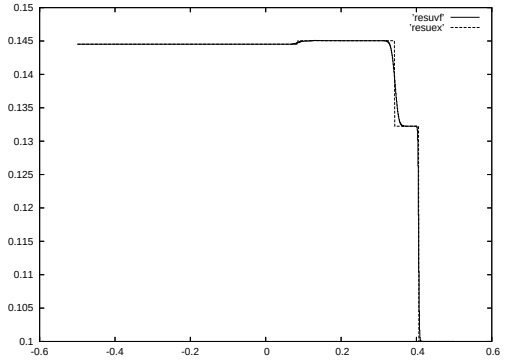
FIGURE 1. HLL scheme and phase transition, $CFL = 0.9418$.



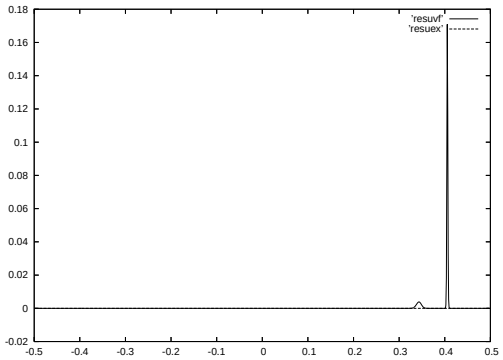
(a) Density



(b) Velocity

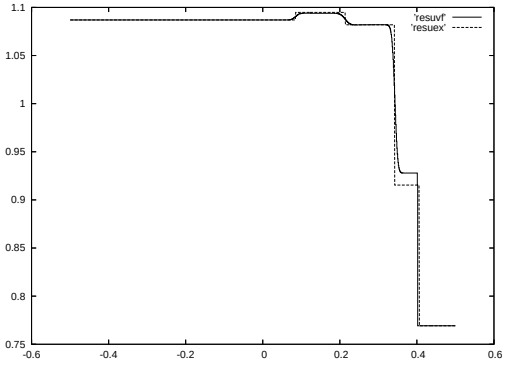


(c) Pressure

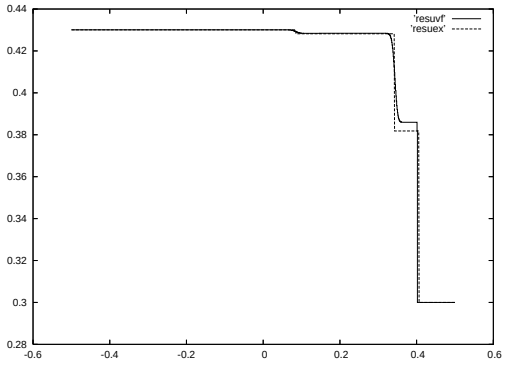


(d) Entropy production

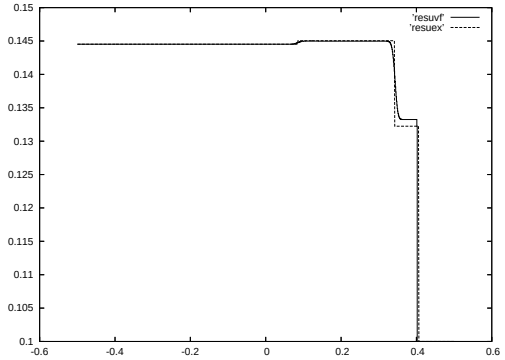
FIGURE 2. HLL scheme and phase transition, $CFL = 0.9419$.



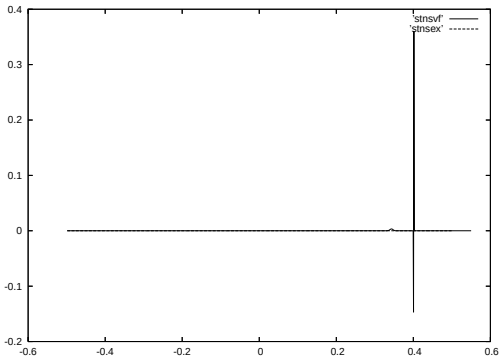
(a) Density



(b) Velocity



(c) Pressure



(d) Entropy production

FIGURE 3. Isotherms of the simple critical model with $\gamma_1 = 1.4$ and $\gamma_2 = 1.1$.